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Title of the proposed thesis:

Studies on Organic Charge-transfer Complexation in terms of Non-covalent Interactions

Synopsis of the proposed research work

1. Origin of the research problem

Charge-transfer complexes are formed by a weak involvement of molecules, one acting as an electron donor and another as an electron acceptor. This type of interactions does not make up a strong a covalent bond and very much dependent on temperature, concentration, and solvent. In 1949 H. Benesi and J. Hildebrand, investigate the charge-transfer interaction of iodine with aromatic hydrocarbon [1]. In 1954, researchers at Bell Laboratories and somewhere reported charge-transfer complexes with resistivities as eight ohm.cm in combinations of perylene with iodine or bromine. In 1962, the well-known acceptor tetracyanoquinodimethane (TCNQ) was reported [2]. Tetrathiafulvalene (TTF) was synthesized in 1970 and found to be strong electron donor. In 1973, it was discovered that a assemblage of these components from a strong charge-transfer complex, henceforth referred to as TTF-TCNQ [3]. The complex is formed in solution and may be crystallized into a well-formed crystalline organic conductor. In a TTF-TCNQ crystal, TTF and TCNQ molecules are arranged independently in separate parallel-aligned stacks.

The first organic molecule that forms a superconductor was discovered in 1980.Tetramethyl-tetraselenafulvalene-hexafluorophosphate ($TMTSF_2PF_6$), a semi conductor at ambient conditions, shows superconductivity at low temperature (critical temperature) and high pressure: 0.9 K and 12 kbar. Unfortunately, critical current densities in these complexes are very small.

CT phenomenon was introduced first by Mulliken and he presented the well- known theory [4] of CT interaction between an electron donor and acceptor molecules, and it has been successfully and widely functional to many interesting research subjects. According to Mulliken's theory chemical intuition is needed to define a 'donor' and 'acceptor' molecule in a CT complex and a linear relationship is expected to exist between the complex formation energy and the square root of the magnitude of charge transferred. On the other hand, the magnitude of the charge transferred depends on the donor–acceptor properties of the system, in which the donor property is determined by ionization potential of the donor and a linear relationship between ionization potential of the donor is expected [5]. The term CT gave a certain type of complex resulting from interactions of donor and acceptor with the formation of weak bands [6,7] and discussed widely by Foster [8]. Molecular interactions between electron donors and acceptors are associated with the formation of intensely colored CT complexes in which absorb radiation is in the visible or UV-vis region [9]. There have been various types of donors and acceptors used in literature for studies of CT complexes [10-17].

2. Objectives(s) of the work

The objective of the proposed work is to carry out the detailed spectroscopic study of complexation of different kinds of electron acceptors with a specific donor in a particular solvent or different solvent. Try to synthesize the crystal of the donor-acceptor complex and its characterization by FT-IR, ^{1}H NMR, and elemental analysis. Thermal stability, the composition of the synthesized complex is determined by TGA-DTA analysis. Finally find out the probable nature of the interaction, electronic properties, etc. by theoretical study mainly density functional theory (DFT) with suitable basis set.

3. Methodology

3.1 Uv-visible spectroscopic study:

To know whether a charge transfer complex is formed or not with the help of absorption spectroscopy the spectrum which exhibits the characteristic absorption band attributed to the charge transfer transition and this band arises due to the transition of an electron from the highest occupied molecular orbital of the donor (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the acceptor. In the UV–vis spectrum of the donor upon the addition of the acceptor and revealed the presence of the new absorption bands that correspond to the CT interactions and emergence of one or more isosbestic point. Stoichiometry of the complexes has to be determined by Job's plot of continuous variation of absorbance. Only those cases in which a CT-complex is formed, the formation constant of the complex are determined by Benesi-Hildebrand equation [18]. Charge-transfer related parameter as like ionization potential of the donor [19], resonance energy [20], free energy [21], oscillator strength [22], and transition dipole moment [23] etc., to be calculated using standard applied equation.

3.2 Fluorescence spectroscopic study:

Detailed emission study of the donor-acceptor systems and their interpretation and calculation of excited state binding constant by Stern-Volmer equation. A variety of processes can result in such decreasing in intensity involving collisional or dynamical quenching, static quenching, FRET, etc. In Static Quenching fluorophores form a reversible complex with the quencher molecule in the ground state. Dynamic quencher occurs in association with a collision between fluorophore in its excited state and quencher molecule. The fluorophore returns to ground state without emission of light. On the other, in static quenching, a non-fluorescent complex is formed between the fluorophore and the quencher. Usually, only a fluorophore which is not complexes can exhibit fluorescence. The fluorophore can form a stable complex with another molecule. If this ground-state is non-fluorescent, then we say that the fluorophore has been statically quenched. In such a case, the dependence of the fluorescence as a function of the quencher concentration follows the relation called Stern-Volmer equation. FRET results in a decrease of the fluorescence

intensity and lifetime of the donor probe; it enhances the fluorescence of the acceptor probe when the acceptor is fluorescent. When the donor molecule absorbs a photon, and there is an acceptor molecule close to the donor molecule, radiation less energy transfer can occur from the donor to the acceptor.

3.3 FT-IR study:

The formation of the intermolecular charge transfer compound is strongly evidenced by the presence of characteristic bands of the donor and acceptor molecules in the spectrum. FTIR spectra of the organic compounds have been obtained in the region 4000–650 cm^{-1} and more important use of the infrared spectrum to determine structural information about a molecule. The main infrared bands of both donor and acceptor are in the complex spectrum with some changes [24-25] in wave numbers or intensities as a result of the change in the electronic structure upon complexation. The appearance of new band or changes of the intensities in the complex spectrum on donor and acceptor ascribed the formation of charge-transfer complexation.

3.4 ^{1}H NMR study:

The NMR technique is used to detect the presence of particular nuclei in a compound for given nuclear species. It is also an important tool for the identification of molecules and for the examination of their electronic structure. ^{1}H NMR spectrum of the CT complex has been observed with some changes in comparison to those of their constituents or emergence of new peak [26].

3.5 TGA-DTA study:

To confirm the composition and structures of the formed solid CT complexes, thermal analyses (TGA and DTA) is a very good tool. The composition and thermal stability of the donor, acceptor and resulting CT complex were obtained by thermo gravimetric (TGA) and differential thermal analysis (DTA).The difference of TGA-DTA plot of solid complex concerning donor and acceptor is the confirmation of CT-complexation [27].

3.6 Theoretical study:

Energy minimized optimization of the donor, acceptor and the formed complex to be done by DFT study with a suitable basis set. The optimized structure of the formed complex showed high stabilization energy in concordance with the high values of formation constant, molecular extinction coefficient, and oscillator strength as well as transition dipole moment. The computed geometrical parameters (bond lengths and bond angles) showed different values for the complex compared with the reactants confirming the CT interaction. Also, the Mulliken atomic charge exhibited high values for the acceptor complex moiety and a decrease in the donor one compared with the acceptor and donor alone, asserting the CT

complex formation. Also the suggested positioning of the acceptor molecule on the donor molecule confirmed theoretically from the HOMO, LUMO and molecular electrostatic potential map calculations of the charge transfer process [28-30].

4. Future prospect

Now days the study of weak interactions is a topic of great interest because these non-covalent interactions are the main key to determining the stability of DNA duplexes, folded states of proteins, enzyme–substrate complexes, and ligand-receptor interactions and rationally design the new drug. Weak interaction plays the pivotal role to recognize a molecule, cation, anion among the various similar types of molecule. So, weak non-covalent interaction is very much necessary for the development of sensing mechanism. Further chage-transfer complex has a lot of application in different field of chemistry as like organic semiconductors [31], solar cells [32], and dendrimers [33], photo-catalyst [34] etc.

5. Reference

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